Review

Foliar heavy metal uptake, toxicity and detoxification in plants: A comparison of foliar and root metal uptake

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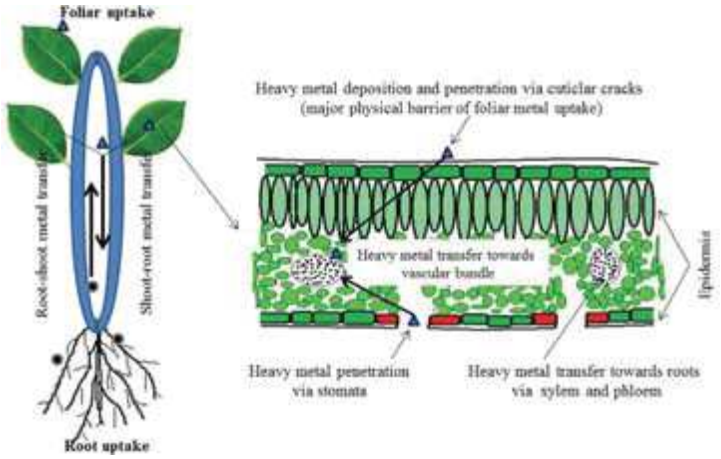
HIGHLIGHTS

- This manuscript reviews foliar uptake of heavy metals by plants.
- Modern development has enhanced atmospheric heavy metal pollution worldwide.
- Atmospheric heavy metals can deposit and enter plants via foliar transfer.
- Atmospheric heavy metals can induce severe health risk by vegetable contamination.
- Unlike root transfer, foliar metal transfer is not well known.

GRAPHICAL ABSTRACT



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ABSTRACT

Anthropologic activities have transformed global biogeochemical cycling of heavy metals by emitting considerable quantities of these metals into the atmosphere from diverse sources. In spite of substantial and progressive developments in industrial processes and techniques to reduce environmental emissions, atmospheric contamination by toxic heavy metals and associated ecological and health risks are still newsworthy. Atmospheric heavy metals may be absorbed via foliar organs of plants after wet or dry deposition of atmospheric fallouts on plant canopy. Unlike root metal transfer, which has been largely studied, little is known about heavy metal uptake by plant leaves from the atmosphere. To the best of our understanding, significant research gaps exist regarding foliar heavy metal uptake. This is the first review regarding biogeochemical behaviour of heavy metals in atmosphere-plant system. The review summarizes the mechanisms involved in foliar heavy metal uptake, transfer, compartmentation,

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Root uptake
Toxicity
Detoxification

toxicity and in plant detoxification. We have described the biological and environmental factors that affect foliar uptake of heavy metals and compared the biogeochemical behaviour (uptake, translocation, compartmentation, toxicity and detoxification) of heavy metals for root and foliar uptake. The possible health risks associated with the consumption of heavy metal-laced food are also discussed.

Contents

1. Introduction

Mineral resources correspond to important material base for socio-economic progress. Notwithstanding, the significance of mineral resources, extraction and use of mineral in different industrial processes have inflicted serious environmental dilemma, especially in term of environmental heavy metal pollution [1–3]. The occurrence of high levels of heavy metals in the environment is a potential threat to human health and the ecosystems [4–6], owing to their toxicity, tendency to bioaccumulate and very high persistence in the ecosystem [1,4–7]. Although some heavy metals such as manganese (Mn), zinc (Zn), chromium (Cr), copper (Cu), iron (Fe) and nickel (Ni) are required as micronutrients for living organisms including plants, they may induce noxious effects at higher levels [7]. Other non-essential metals induce severe toxicity to living organisms even at low applied levels, such as mercury (Hg), cadmium (Cd), arsenic (As) and lead (Pb) [7–9].

Due to rapid and uncontrolled industrialization and urbanization along with rigorous farming, the global environment has been under considerable pressure. Modern development released a number of toxic pollutants to the atmosphere through numerous human activities [10,11]. According to Chmielewska et al. [12], heavy metal emission to atmosphere by anthropogenic activities is up to several times higher than their natural emissions. Industrialization is characterized by significant emissions of heavy metals into the atmosphere [13,14], and has a serious threat to human health and terrestrial ecosystem [9], mainly in mining and industrial areas [15,16]. Metals are emitted to the atmosphere by both anthropogenic and natural sources [7,17]. Unfortunately, numerous cases of atmospheric contamination exist nowadays [14,18] and heavy metals are still emitted to the environment worldwide [7,16]. Heavy metals released into air from natural or anthropogenic sources can transport over long distance. Therefore, enhanced levels of heavy metal have been commonly described in atmosphere [19,20], soil [21–24], crop [25–28] and water reservoirs [29–31] near urban areas or sites adjacent to industrial units. Exposure to persistent and toxic heavy metals adsorbed onto atmospheric dust particles can be a severe possible human health risk [32]. For that reason, it is necessary to assess the potential environmental and human health risks associated with the atmospheric transport of heavy metals emitted from smelter and other industrial activities onto a large geographical area [29].

Health hazards allied with these atmospheric pollutants may arise primarily from inhalation of atmospheric dust particles and ingestion of polluted crops/vegetables mainly in urban areas with high population density [33]. Studies dealing with the uptake and accumulation of heavy metals by crops/vegetables have examined metal accumulation via root system only [3]. It is because majority of the heavy metals build-up in the soil system, and are absorbed by plants mainly via root system. In addition to plant roots, the aerial organs of plants such as leaves, fruits and flowers can also absorb heavy metals [34]. This implies that plant aerial organs are efficacious absorbing structures equipped with heavy metal uptake mechanisms similar to the roots. Actually, metals can be

accumulated in plant leaves through foliar transfer after deposition of atmospheric particles on the leaf surfaces [16,25]. Plants growing near mining and smelting areas as well as in urban areas display increased foliar concentrations of heavy metals [14,16,35]. Therefore, biomonitoring studies near industries or roads currently receive greater attention to evaluate metal contamination via atmospheric deposition/transfer.

Unlike root metal transfer, which has been largely studied [36], less research has been focussed to explore and examine about heavy metal uptake by plant leaves from the atmosphere [18,37,38]. Furthermore, most of the studies on metal uptake are not recent and generally focused on metal concentration without investigating the transfer pathways involved [39–43] or have solely focused on fallout biomonitoring [25,44–46]. Foliar absorption of heavy metals has been primarily evaluated for those metals which have well-known essential roles in the metabolic and biochemical reactions of plants. For example, several previous studies reported about foliar absorption of Fe, Cu, Mn and Zn [42,47–49]. It is well-established that these metals can penetrate on cuticles and finally accumulate by the underlying tissues of plant leaves [50]. The non-essential metals such as lead (Pb) [35,42], cadmium (Cd) [42,51], chromium (Cr) [52] and arsenic (As) [16,53,54] can also enter plant leaves via foliar transfer.

Despite considerable progress in recent years about foliar absorption of heavy metals by plants, there exist a gap of knowledge and the topic is still newsworthy. To the best of our knowledge, there is no comprehensive review available regarding biogeochemical behaviour of foliar heavy metal uptake. The current review therefore summarizes: (i) mechanisms involved in foliar heavy metal uptake by plants; (ii) factors affecting foliar heavy metal uptake; (iii) transportation, speciation and compartmentation of heavy metals inside plants after foliar uptake; (iv) toxicity and detoxification of heavy metals after foliar uptake, and (v) comparison of root and foliar uptake of metals.

2. Atmospheric pollution by heavy metals: a global concern

Earth's atmosphere mainly consists of oxygen (O_2), nitrogen (N_2) and carbon dioxide (CO_2). However, rapid economic development, urbanization, and industrialization during the last 3–4 decades significantly deteriorated the quality of atmosphere by emitting various pollutants. The common organic and inorganic atmospheric pollutants include ozone (O_3), sulfur dioxide (SO_2), nitrogen oxides (NOx), CO_2, hydrogen fluoride (HF), carbon monoxide (CO) and formaldehyde (HCHO) [10,11,55]. Heavy metals are emitted to the atmosphere by various anthropogenic sources (Table 1). Heating of ores in metal processing smelters emit large quantities of air contaminants, and a variety of heavy metals into the atmosphere [29]. Besides, some suspended particles (solid and liquid) in the air termed as particulate matter (PM) or aerosols also represent serious environmental threats. Heavy metals may be emitted to atmosphere as volatile compounds or very fine particles either as "fugitive" releases from general industrial processes or via chimneys [29,56–58] (Table 1). Industrial emitted heavy metals such as As, Cr, Pb, Ni, zinc (Zn), Cd and vanadium (V) are carcinogenic [7]. In particular, As, Cd, Pb, Cr, and mercury (Hg) are among the most toxic heavy metals with respect to their potential toxicity and exposure to living organisms. Goix et al. [2] evaluated ecotoxicity, human bioaccessibility, cytotoxicity, and oxidative potential of heavy metals emitted into the atmosphere and reported following order of the hazard classification: $CdCl_2 > CdO_4 > CuO_4 > PbO_4 > ZnO_4 > PbSO_4 > Sb_2O_3$.

Atmospheric pollution by heavy metals is caused primarily by stationary or mobile sources, such as waste incineration, domestic oil burning, power generation plants, industrial units, vehicular traffic, and the resuspension/remediation of contaminated sites [59]. Among these, heavy metal emission from industrial and traffic activities represent the most important sources of atmospheric pollution [20,60]. Smelters and industrial plants that involve burning of ore such as refuse and waste incinerators, coal-fired units can emit comparatively high quantities of metals into the atmosphere [29,61]. Emissions of heavy metals to the air by industrial processes occur via crushing, fusion, reduction, refining and processing [15,62]. Once in the atmosphere, the mobility of heavy metals is high: the pollutants can easily move on several kilometers in function of wind design. Even the uncontrolled waste incineration in small house boilers contributes towards air pollution by heavy metals. Elevated levels of atmospheric heavy metals compared to prehistoric levels are especially reported in European countries during last several decades. Almost 108 and 4800 t of Pb were emitted into the atmosphere respectively in France and Europe [25], primarily as PM released by Pb production and acid battery recycling plants [15,63].

Heavy metal levels in atmosphere vary greatly between urban and rural areas, as well as with distance from emission sources, such as metal smelters and coal burning in power plants [18]. For example, airborne levels of As range from 10 to 200 ng/m^3 in urban areas, while–10 ng/m^3 in rural areas [64]. Arsenic concentration may exceed 1 $\mu g/m^3$ near emission sources. The mean atmospheric level of As was reported to be 3.25 ng/m^3, 5.3 ng/m^3, and 4.3 ng/m^3 in Washington DC, Toronto and Chicago, respectively [65]. In Germany, average As level in atmosphere ranges from 5 to 20 ng/m^3 [66].

Annual mean level of Pb in cities ranges between 0.2–0.6 $\mu g/m^3$ in eastern Europe and <0.1 $\mu g/m^3$ in western Europe. The mean Pb atmospheric level was 0.05 $\mu g/m^3$ in Lisbon[64]. Mean annual atmospheric Cd concentrations were about 0.1 ng/m^3, 0.1–0.5 ng/m^3 and 1–10 ng/m^3 respectively in remote, rural and industrial areas during 1980–1988, in the northern European countries [64]. Cadmium atmospheric concentrations in cities ranged from 6 to 360 ng/m^3, 2–50 ng/m^3, and 10–53 ng/m^3 respectively in the USA, Europe and Japan.

In the ambient air, Hg levels of European Community vary from 0.001–1.0 ng/m^3 in urban areas and up to 20 ng/m^3 in industrial areas [64]. Nickel levels in atmosphere range from 1 to 10 ng/m^3 in urban areas [64], but in large cities and near industrialized areas Ni level in air may reach 170 ng/m^3 [67]. Thurston and Spengler [68] showed Ni levels of 8.57 ng/m^3 and 2.44 ng/m^3 respectively for $PM_{2.5}$ and $PM_{1.5\text{-}2.5}$ in the suburb of Boston. Heavy metal levels in air vary in different countries (Table 2), which mainly depend on the intensity of industrialization and urbanization.

3. Atmospheric pollution by heavy metals and particulate matter

After emission, heavy metals may attach with various atmospheric particles [69] (Table 1). For example, Norouzi et al. [32] reported that majority of the heavy metals co-exist with atmospheric particles due to the integration of these metals into the matrix structure during incineration process or adsorption onto the surface of ferri-magnetics found in the atmosphere. Particulate matter includes complex mixture of various particles in atmosphere, numerous of which are harmful. The reactivity of PM with respect to bioavailability and toxicity is higher than coarse emissions. Therefore, it can persuade sever sanitary [20] and environmental concerns [15,16]. Thus, many atmospheric pollution assessment studies have been carried out in many regions to analyze the chemical composition [70], spatial and temporal variation of PM [71], and the levels of human exposure [72]. Numerous previous reports indicate that organic and/or inorganic colloids of

Table 1
Heavy metal emission (tons) from different sources into the air.

Industrial activity	Cd	Hg	Pb	As
Energy sector	5.72	19.8	80.9	2.069 t
Mineral oil and gas refineries	1.09	1.04	2.14	1.63 t
Thermal power stations and other combustion facilities	3.72	18.50	61.1	205 t
Coke ovens	1.01	0.28	17.4	–
Production and processing metals	9.66	4.77	398.3	–
Mineral industry	1.79	4.00	60.9	1 t
Chemical industry	0.72	6.14	2.34	–
Waste and waste water treatment	0.24	1.22	5.41	0.3 t
Paper and wood production processing	0.56	0.22	3.17	9 t
Animal and vegetable products from the food and beverage sector	0.05	–	–	–
Other activities	0.03	0.01	–	–
Total	25	56	632	219 t

Source [318].

Table 2
Heavy metal levels in air reported in different countries.

Country	Poland	Pakistan	Spain	Algeria	Iran	India	UK	Nigeria
Metal	[319] Concentration in air (ng/m^3)	[320] Concentration in air (ng/m^3)	[321] Concentration in air (ng/m^3)	[322] Concentration in air (ng/m^3)	[323] Concentration in air (ng/m^3)	[324] Concentration in air (ng/m^3)	[325] Concentration in air (ng/m^3)	[326] Concentration in air (ng/m^3)
Pb	23.6	16.24	9.24	299	120.92	–	10.22	0.832
Cd	0.806	31.66	0.25	21.2	0.33	0.02	0.2	–
Zn	66.5	0.85	354	–	164.58	7.13	–	1.712
Ni	2.15	65.78	3.38	42.4	5.33	0.29	1.74	0.478
As	0.534	–	0.55	–	7.77	–	0.91	–
Fe	–	–		639.8	652.41	20.81	–	1.081
Co	0.271	12.69		37.7	5.13		–	–
Al	0.058	3.01	–	–	241.51	13.89	–	–

varying sizes (1–1000 nm) in the atmosphere as well as in different compartments of the environment such as soils, lakes, streams, groundwater, rivers, and oceans play key role in the biogeochemical cycle/circulation of pollutants [73,74]. Particularly, mineral nanoparticles in the atmosphere have been found during the course of evolutionary change of hominids, and human exposure to these heavy metals via dermal, inhalation, and ingestion pathways are imperative foci of nanotoxicology [75]. It is reported that environmental nanoparticles possess high sorption capacity for As, Zn, and Pb [76]. For example, 12-nm magnetite particles were almost 200folds more effective than 20 and 300 nm particles, in removing As(V) and As(III) from water [77].

The epidemiological reports have presented a strong relationship between elevated levels of inhalable PM (mainly of size PM_{10} and $PM_{2.5}$) and enhanced morbidity and mortality [78–81]. Particulate matter is especially considered a serious health hazard because of its very small size which can be inhaled deeply into the lungs, and occasionally even into the blood circulation. Several previous studies around the globe has described that both short-term and long-term exposures to atmospheric heavy metals can induce severe health effect to the local habitants and are associated with enhanced morbidity and mortality [82]. In 1952 (between December 5–9), around 4000 people died in London as a result of illnesses associated with respiratory diseases such as pneumonia and bronchitis. Similarly, another 8000 deaths were caused because of smog's effects caused over the next few months [83]. Samples collected from victims showed that lungs were contaminated with high levels of very fine particles, including heavy metals such as Pb, Zn, and Fe. Keeping in view these health issues associated with atmospheric fine particles, the US Environmental Protection Agency set exposure level for PM_{10} micrometers or less in 1987, and for $PM_{2.5}$ micrometers or less in 1997.

The fraction of different heavy metals attached with different PM varies with metal type. Dubinskaya [84] reported that 75% portion of PM_2 contains elements such as Cu, cesium (Cs), Zn, As, Cd, and Pb in the gases emitted from waste incineration furnaces. For example Pb was 0.58% of mass fraction in the PM_1, while only up to 0.40% in the PM_{10}. On the contrary, Cu, Mn and Fe are mainly attached with PM_{10} fraction compared to PM_1. The attachment of heavy metals with different size of PM also varies with the type of origin source. Canepari et al. [85] reported heavy metal distribution in coarse (>2.5 μm) and fine (<2.5 μm) PM in Rome-Italy, and found that heavy metals such as calcium (Ca), barium (Ba), iron (Fe), magnesium (Mg), and manganese (Mn) were mostly in the coarse fraction, whereas elements of anthropogenic origin, i.e., vehicle emissions, non– tailpipe traffic sources, and railway emissions were found in the fine fraction. They reported that >50% of the total concentration of Pb and Cd being in the size fraction <1 μm. Investigations of atmospheric $PM_{2.5}$ and PM_{10} in Hong Kong also reported similar observations [86,87].

Table 3
Health risk guideline values in ambient air for different heavy metals (Source WHO) [89].

Substance	Time-weighted average	Averaging time
Cadmium	5 ng/m^3	Annual
Lead	0.5 μg/m^3	Annual
Manganese	0.15 μg/m^3	Annual
Mercury	1.0 μg/m^3	Annual
Nickel	0.5 mg/m^3	Many years
Arsenic	5 ng/m^3	–

4. Foliar deposition and uptake of heavy metals

Heavy metals emitted from industrial smelters are transported up to several kilometres away from their sources by wet or dry deposition [14,88]. The presence of heavy metals in air can induce numerous health risks to target organisms. Word health organization (WHO) has established health risk guidelines of heavy metals in ambient air (Table 3) [89]. These metals can be accumulated in

plant leaves through foliar transfer after deposition of atmospheric particles on the leaf surfaces [25]. The potential of plant foliar parts to absorb nutrients, water and metals was documented about three hundred years ago [90]. Unlike root metal transfer, which has been largely studied [91], little is known about metal uptake by plant leaves from the atmosphere [18,37,38]. Furthermore, most of the studies on metal uptake via foliar transfer are not recent, and have not investigated the transfer pathways involved [40,43] or have solely focused on fallout biomonitoring [25,44,46].

According to the pollution context, the foliar transfer of metals can be neglected, or in contrast appears as the main pathway of pollution, particularly when ultra-fine particles interact with plant leaves [92,93]. The plant canopy serves as an efficient filter of atmospheric heavy metals emissions [94]. Several recent and old studies reported that plant canopy can efficiently adsorb and reduce PM ratio in the atmosphere by capturing the airborne PM on their foliar parts [95–97]. For example, a pine forest can retain about 36.4 t ha^{-1} per year of air borne dust [98]. In the city of Zhengzhou-China, vegetation retained about 8600 t yr^{-1} of dust particles in an area of 103 km^2 [99]. Similarly, a shelter belt of trees can retain 38.9–46.1% of dust particles [99]. Liu et al. [100] showed that in Guangzhou-China, 52×10^5 t above ground biomass of urban vegetation with a total leaf area of 459 km^2 can retain 8012.89 t per year of atmospheric dust.

Several previous reports indicated that plants and vegetables growing near smelters show high foliar levels of heavy metals [14,101] (Table 4, Fig. 2). As a result, heavy metal levels in foliar plant organs are frequently described in environmental risk assessment studies [25,27,35], representing as indices of atmospheric pollution load. For example, in industrial areas, heavy metal concentrations in crop plant tissues have been reported several folds higher than the threshold levels [102–105]. Many other studies also reported enhanced levels of heavy metal in foliar plant organs near roadside or industrial areas in France (50–400 lg/g Pb) [106], Bahrain (9–420 lg/g Pb) [107], and Canada (100–3000 lg/g Pb) [108]. Schreck et al. [25] reported Pb accumulation by *Lactuca sativa* L. near secondary Pb-recycling plant, STCM (Chemical Metal Treatment Company), situated in Toulouse, south-western France. Corredor et al. [109] demonstrated accumulation of Fe in *Cucurbita pepo* after foliar application. Xiong et al. [16] showed foliar accumulation of Cd, antimony (Sb), Zn and Pb by *Spinacia oleracea* and *Brassica oleracea* near a smelter. Schreck et al. [25] showed foliar uptake of Zn, Cu, Sn, Cd, tin (Sn), As, and Pb by various vegetable species (*Lactuca sativa, Petroselinum crispum* and *Lolium perenne*) emitted from a battery-recycling factory in France. Uzu et al. [18] reported accumulation of Pb by *Lactuca sativa* after 43 days exposure in the courtyard of a secondary Pb smelter in France. Schreck et al. [93] also reported accumulation of Pb by *Lactuca sativa* and *Lolium perenne* when exposed to Pb-rich particles emitted by a Pb-recycling factory.

Some studies reported the contamination of kitchen garden near industrial areas as a result of deposition and uptake of heavy metal enriched PM [110–112]. According to Uzu et al. [18], foliar absorption of metals due to PM depositions can greatly enhance metal levels in plants, particularly when farms or kitchen gardens are near smelters or recycling plants. Mombo et al. [113] reported enhanced levels of Pb and Cd in vegetables grown in urban gardens.

Heavy metal uptake by foliar surfaces occurs through stomata, cuticular cracks, lenticels, ectodesmata and aqueous pores [49,114]. In fact, absorption of foliar-deposited heavy metals takes place mainly through ectodesmata, which are non-plasmatic channels positioned mainly between subsidiary cells and guard cells in the cuticular membrane or epidermal cell wall. Moreover, the cuticle present above the guard cell is comparatively more permeable compared to epidermal cells. Uzu et al. [18] showed that PM adsorbed on plant leaves is mainly retained by trichomes and cuticular waxes, but some of metals linked to PM can enter inside plant leaf tissues. Foliar uptake of metals is considered a surface phenomenon [34]; however, the adaxial cuticular features are key in assisting high metal absorption via adaxial surfaces. Kozlov et al. [115] studied the transfer of Cu and Ni-rich particles in birch, and suggested that particles may enter inside plant leaves through stomata. Fernandez and Eichert [90] proposed that particles could enter inside the leaf tissue via pores present on the leaf cuticle and inside stomata. Like root uptake, foliar uptake of heavy metals may also occur in a dose dependent manner. For example, Kozlov et al. [115] reported linear relationship between Ni contents in the leaves and Ni contents in moderately and heavily polluted sites at the Kola Peninsula, Russia. Similarly, a linear relationship was reported between foliar applied As level and As uptake by the fronds [34].

Therefore, it is highly necessary to assess the risk for human health due to consumption of polluted plants after foliar uptake. However, there exist very rare data regarding health risks in kitchen gardens/farms near atmospheric contamination sources [113].

4.1. Use of lichen as bioindicator of atmospheric heavy metal pollution

Lichens have been frequently used to biomonitor atmospheric levels of pollutants including heavy metals originating from the anthropogenic sources such as smelters, power plants, auto-

Table 4
Foliar heavy metal uptake by vegetables and associated health risks near industrial areas.

Metal	Reference	Vegetable	Concentration in atmospheric fallouts (mg cm^{-2})	Concentration in plant shoot (mg/kg)	Concentration in grains	GEF	DIM (mg kg/day)	HRI
Cd	[16]	Spinach		317.3	–	396.6	0.127	25.493
Cd	[327]	Rice		30.1	2	0.1	0.012	2.418
Cd	[25]	Lettuce	0.9	1.7		1.9	0.001	0.137
Pb	[18]	Lettuce		335		300.1	0.135	26.915
Pb	[93]	Lettuce		171.5		248.7	0.069	13.779
Pb	[25]	Lettuce	456.2	122		0.3	0.049	9.802
Pb	[16]	Spinach		485	–	79.5	0.195	38.966
Zn	[25]	Lettuce	6.9	29.1		4.2	0.012	2.338
Zn	[328]	Wheat		31.68	43.61	1.4	0.013	2.545
Zn	[16]	Spinach		144.2	–	5.7	0.058	11.585
Zn	[329]	Wheat		86.8	43.4	0.5	0.035	6.974
Sb	[25]	Lettuce	1.9	1.4		0.7	0.001	0.112
Sb	[16]	Spinach		276.3	–	50.2	0.111	22.199
Ni	[115]	Birch	58.2	4.8		0.1	0.002	0.386
Cu	[25]	Ryegrass	1.7	7		4.1	0.003	0.562
As	[25]	Lettuce	0.2	1.1		5.5	0	0.088

GEF; Global Enrichment Factor, DIM; Daily Intake of Metals, HRI; Health Risk Index.

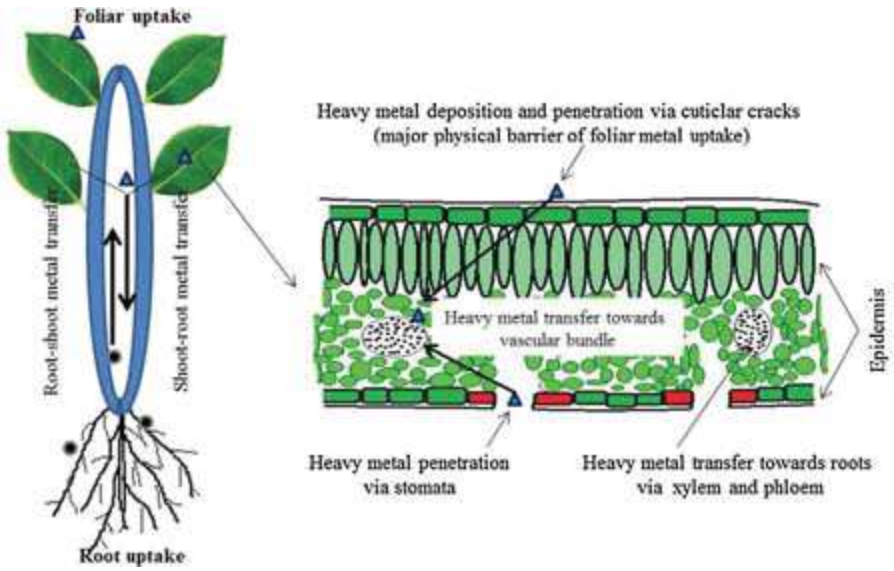

Fig. 1. Foliar pathways of heavy metal entrance to plants.

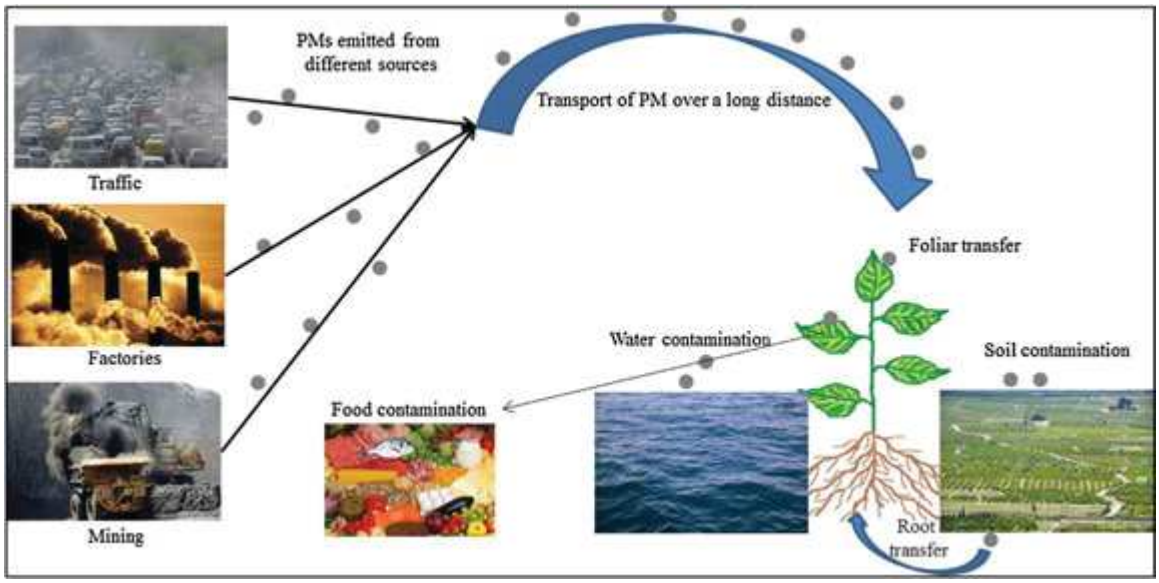

Fig. 2. Heavy metal emission into atmosphere from different industrial activities, transfer over long distances in air, deposition and absorption by plant foliage, and possible risks of food chain contamination.

mobiles, agriculture and industries (Table 5, Fig. 3) [116–119]. Epiphytic lichens diversity ascertained to be suitable and the strong indicator of air quality [120]. Air quality monitoring more often uses the macrolichens which are lichens with fruticose and foliose life form. Beyond simple mapping of the pollutant levels in the atmosphere, researchers have revealed correlations between the lichen bioindicators and locally elevated levels of the serious illnesses including cancer [121]. Lichen biomonitoring by various methods may be applied including the assessments of species abundance, health and diversity, isotopic and chemical composition. Where lichens are not present naturally, transplants lichens may be used.

Lichens intercept the atmospheric pollutants associated with dry depositions, wet precipitation and gaseous emission [122]. The physiology of lichens favors enhanced absorption of atmospheric pollutants from the air through the entire surface [46]. This feature is associated with their ability to accumulate airborne particles. Unlike flowering plants, mostly lichens have no outer protective waxy cuticle and no special organs for the water absorption,

Table 5
Concentration (μg/g DW) of heavy metals in bioindicator plants (lichen and mosses) of air quality.

Plant species	Plant	Heavy metal	Concentration	References
Lichen	*Parmelia carperata*	Zn	59.85	[330]
	Lecanora muralis	Pb	4427	[331]
	Hypogymnia physodes.	Cu	9	[332]
	Phaeophyscia hispidula	As	68.3	[333]
	Hypogymnia physodes	Pb	34.7	[334]
	Pyxine cocoes	Cd	16.9	[333]
	Phaeophyscia hispidula	Zn	1248	[333]
	Hypogymnia physodes	Ni	3	[334]
Mosses	*Hylocomium splendens*	Ni	15.8	[335]
	Fabriona ciliaris	Zn	136.8	[336]
	Sphagnum papillosum	Pb	6.6	[335]
	Racopilum africanum	Ni	23.78	[330]
	Thuidium tamariscinum	Cd	0.44	[335]
	Sphagnum papillosum	Cd	4.31	[337]
	Hylocomium splendens	Pb	458	[338]
	Pleurozium schreberi	Zn	170	[334]

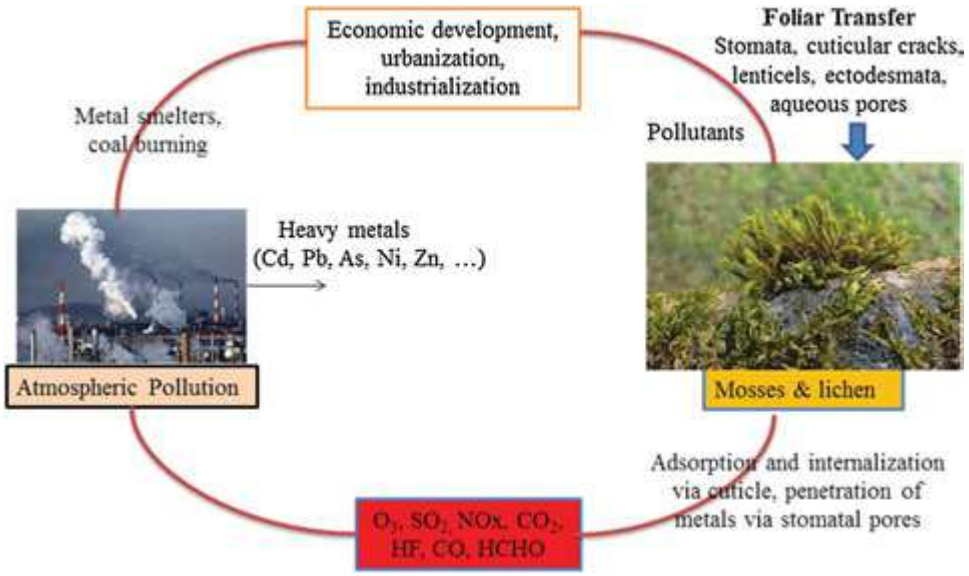

Fig. 3. Foliar heavy metal uptake by mosses and lichen.

therefore absorb gases and particulate matter from environment passively [123]. Heavy metals concentrations in the lichen thalli correlate with their atmospheric levels [124,125]. The capacity of lichen to accumulate higher amount of trace elements and the sensitivity to them depend on the specie of lichen and they are given by structural and morphological characteristics thereof [126,127]. Few lichen-based studies reported biological effects of the atmospheric pollution evaluated by various waste management/remediation techniques such as landfilling, waste incineration, and industrial composting [128–132].

Two mechanisms in the lichen thallus can explain the pollutants accumulation mechanism:

(1) extracellular binding of cations;
(2) PM adsorbed onto thallus surface and penetration to intercellular spaces [116,117].

4.2. Use of mosses as bioindicator of atmospheric heavy metal pollution

Mosses have been used in national surveys and case studies of heavy metal atmospheric pollution around the industrial sites (Table 5, Fig. 3) [118,133–136] for the estimation of long term and spatial trends in the deposition of metal such as in the International Cooperative Program on Effects of Air Pollution on Natural Crops and Vegetation or ICP Vegetation [137].

In Europe, use of terrestrial mosses as a bioindicator of atmospheric metal pollution deposition from ambient air has been reported since late sixties. Due to widespread presence, lower cost and high adsorption capacity of pollutants, terrestrial mosses are used more commonly than other sorbents. For atmospheric biomonitoring, the most commonly used method is "moss-bag technique" [138,139]. Bryophytes, particularly mosses have been used since 1970s to monitor the ecosystem exposure to the several pollutants including persistent organic pollutants, trace metals and excess nitrogen. First, bryophytes lack vascular system and lack developed root system, thus mosses likely take up most of the nutrients from water that contacts their branches or leaves directly.

Mosses generally accumulate water from rainfall making mosses a useful tool for the assessment of biological exposure to the atmospheric deposition. However, several studies indicated that mineral elements can be extracted from soil by some mosses [140,141] although in comparison with atmospheric inputs, soil nutrient inputs seems minor. The abundant biomass of mosses and ubiquity in various ecosystems and also throughout the world make them a convenient bioindicator. Mosses are capable of accumulating large quantities of heavy metals leading to the higher concentrations of element in mosses than in rainfall or air.

5. Mechanisms of foliar uptake of heavy metals

Although partially understood, it is essential to knock down the translocation mechanism of metal throughout the plant, which takes place after foliar absorption of heavy metals by plant leaves. Different authors proposed different mechanisms of metal/nutrient entrance to plant via foliar transfer. Generally, foliar uptake refers to enhanced metal contents in foliar tissues, but it is not easy to differentiate between these steps of foliar metal uptake and transfer inside the plants. Schreck et al. [111] described that two major steps involved in foliar metal uptake include: (i) adsorption and internalization via the cuticle; and (ii) penetration of metals via stomatal pores (Fig. 1).

Heavy metal deposition onto plant leaves is referred via three mechanisms: chemical, physical and biological [142]. The physical adsorption of metals is related to the mechanical capture of heavy metal containing PM by the foliage, taking into account the physical characteristics of vegetation. The chemical and biological factors of heavy metal adsorption take into account the initial retention/deposition of metals by plant cuticle. Moreover, the permeability of the cuticle and chemistry of the heavy meals also govern heavy metal adsorption on plant leaves. Recently, Birbaum et al. [143] described that fine particles penetrate inside the leaves, while large particles are stuck on the surface wax. Dust particles containing metals are generally trapped by the cuticular wax and then diffused into the leaves. Soluble compounds interact directly with the cuticle, which is a waxy layer and confers a hydrophobic feature to the surface of plants. The degree of polarity and hydrophobicity of plant surface varies with plant species.

Plant cuticle contains functional moieties such as carboxylic moieties and therefore acts as a polyelectrolyte [114]. The configuration of the bio-polymer matrix varies with the type of plant genotypes, species and organ, growing conditions and stage of development [144]. Moreover, surface treatments such as silicon (Si) or low weight organic compounds addition (elicitors) can mod-

ify the phyllosphere characteristics and reactivity. According to Chamel et al. [145], heavy metal penetration via leaf cuticle mainly involves four steps:

(i) adherence to the cuticle;
(ii) penetration through the cuticle (possibly via endocytosis);
(iii) desorption in the apoplast;
(iv) absorption by the subjacent cells.

Several metals such as cobalt (Co), Cu or Mn could cross the plant cuticle of aerial organs [43]. However, penetration through cuticle depends on the size of PM and/or heavy metal. For instance, Eichert et al. [146] showed that small size nanoparticles of Cu (43 nm) penetrated leaves of *Vicia faba*, while larger particles (1.1 μm) were unable to penetrate through stomata. Grantz et al. [147] suggested that PM deposition could involve vegetative surface injuries and the uptake of materials, such as metals, across the cuticle. According to Nair et al. [148], heavy metal penetration phenomenon depends on cuticle maturity and environmental factors. The thickness of the organic layer above the internalized primary compounds (about 5 nm) indicates that the process could be a kind of internalization throughout the cuticle wax. Birbaum et al. [143] reported that wax lipids may quickly adsorb on the large surface of the particles. This hypothesis was confirmed by Schreiber [149], who reported polar pathway of penetration across plant cuticles, suggesting a new way for the uptake of ionic compounds. After diffusion/penetration, metal are generally transported via active transport inside the cells symplastic pathway [150]. Active transport of heavy metals inside plants greatly depends on biochemical and metabolic processes of plants [151].

It has been suggested that heavy metals can penetrate the cuticle via two distinct pathways: one for lipophilic and another for hydrophilic substances [152]. The hydrophilic substances penetrate in cuticle via stomata and aqueous pores of the cuticle, while lipophilic substances diffuse through the cuticle [153,154]. For example, the coating of Ag-NPs by cuticular waxes increases their lipophilicity and favors their transfer through the cuticle [154]. Generally, these two pathways of cuticle penetration are described for fine particles [90]. Xiong et al. [16] suggested that small particles might diffuse through both the stomatal and cuticular pathways to enter inside plant leaf. Penetration through stomatal pathway is generally easier because the cuticle of the sub-stomatal cells is comparatively thinner compared to external one [155].

6. Factors affecting foliar absorption of heavy metals

Heavy metal uptake by foliar pathways greatly depends on various factors, such as the physico-chemical characteristics of the cuticle and metals, the morphology and surface area of the plant leaves, the chemical and physical forms of the adsorbed metal, surface texture of leaves (pubescence and roughness), plant habitus (deciduous or evergreen), exposure duration, environmental conditions and gas exchange [156,157]. The deposition and adsorption of heavy metals on plant leaves greatly vary with level of heavy metals in atmospheric PM.

6.1. Effect of heavy metal speciation on their foliar uptake

Nowadays, metal speciation is considered as a subject of significance because of the high variances in the biogeochemical behavior of different chemical forms of a metal [158–160]. It is reported that the heavy metal speciation governs biogeochemical behavior of metals in ecosystem: uptake, toxicity, compartmentation and detoxification inside plants [161,162]. In fact, different forms of a metal vary in their capacity to enter plants via foliar or root uptake. Therefore, it is highly practical to understand the role of metal speciation when assessing the health risks associated with ingestion of vegetables grown in urban vegetable crops or kitchen gardens.

Most available studies on foliar metal uptake deal with the total metal quantity present in ambient air or metal contents in foliar plant tissues, however, only a few focuses on air quality with respect to metal speciation. Uzu et al. [163] evaluated Pb speciation in process PM sampled from various origins; furnace and refining PM. They reported that all PM contained the same major phases of Pb (Pb, PbS, PbO, $PbSO_4$ and $PbO{\cdot}PbSO_4$). They reported high $CaCl_2$ extractable Pb concentration (40 mgL^{-1}) due to high Pb content in PM. They observed that the metal extractability increased with decreasing size of PM.

Similarly, some studies reported that the speciation of metals in air varies with the size of PM to whom these metals are adsorbed in air. For example, Uzu et al. [63,164,165] reported that the process PM collected from the furnace of a secondary lead smelter, located in the urban area of Toulouse-France contains particles with the following diameter distributions: 9%, 50%, 20% and 21% in the PM > 10, PM_{10}, $PM_{2.5}$ and PM_1 fractions, respectively. Using X-ray powder diffraction (XRD) and Raman spectroscopy, Uzu et al. [63] reported that the speciation of Pb was in following decreasing order of abundance: PbS, $PbSO_4$, $PbSO_4{\cdot}PbO$, α-PbO and Pb^0. It is reported that the metal speciation may change after interaction with plant leaves [166]. However, there exist almost no data regarding the effect of metal speciation in PM on its foliar uptake by plants.

6.2. Effect of plant morphological characteristics on foliar uptake of heavy metals

Several recent and old studies tried to understand and characterize the potential mechanisms of heavy metal penetration via foliar uptake. Under identical climatic conditions, different plant species show dissimilar metal retention/adsorption and foliar absorption capabilities. Heavy metal foliar uptake varies with the structure of plant canopy, leaf inclination angle, branch density, as well as factors such as leaf lamina morphologic anatomical parameters of leaves structure characteristics and leaf area [167,168]. Barber et al. [169] described that various plant characteristics affect the atmosphere–plant transfer such as leaf longevity, cuticular structure, leaf surface area and functional type. Among various factors, the size and density of stomata and the leaf surface are the most important factors governing the extent of adsorbed dust/PM and heavy metal [170]. Rao and Dubey [171] reported that morphological factors such as stomatal index and trichome density and length affect the efficiency of dust collection by plants.

Previous studies of have shown that different plant species vary for their capacity to uptake metal via foliar transfer [172]. Tomasevic et al. [37] found that the amount of particles deposited on leaves was dependent on the type of plant species due to different characteristics of the epidermis. Schreck et al. [93] showed that a four-fold higher Pb concentration was observed in the leaves of *Lolium perenne* as compared to *Lactuca sativa* under foliar metal transfer. Qiu et al. [173] reported that the atmospheric PM-retention capabilities of four trees reduced as followings: *Ficus altissima* > *Ficus virens* > *Ficus microcarpa* > *Bauhinia blakeana*. *Lolium perenne* was classified as a good bioindicator for heavy metal atmospheric pollution [174]. Simon et al. [175] reported that the concentrations of Cd, Cu, K, Mg, St and Zn under foliar deposition were significantly lower in leaf tissues of *Pityriasis alba* compared to *Acer pseudoplatanus*. Baycu et al. [176] described higher Cd and Zn levels in *Populus ciliata* leaves compared to *Acer palmatum* under foliar application. This can be due to higher stomatal density of *Acer palmatum* species compared to other plant species. Some authors proposed that stomatal index can be a suitable indicator of atmospheric-plant heavy metal transfer [177].

The physical and physiological features of a plant species greatly influence the potential of plant foliage to adsorb and uptake atmospherically deposited PM and heavy metals. For example, concerning leaf surfaces, some characteristics such as stomatal density, roughness, trichomes, specific leaf area and epicuticular waxes may affect deposition of heavy metals on leaf surface [178]. As reported by Schreiber and Schönherr [179], specific leaf surface areas could elucidate variances in rates of metal uptake between plant species. It is reported that plants having leaves with rough surface and smaller size are capable to adsorb more dust particles than leaves with smooth surfaces and larger size. According to [180], Si was largely present in *Lolium perenne* leaves due to its rough surface. Although *Petroselinum crispum* is hairless as well, it forms a rosette of tri-pinnate finely cut leaves. Ward and Savage [181] measured the Pb content in various plants exposed to road traffic emissions. They observed the same order for Pb contents in plants: grass > aromatic plants > leaf–vegetables > cereals > fruits. Qiu et al. [173] showed that the dust-adsorption abilities of *Bauhinia blakeana*, *Ficus virens*, *Ficus altissima* and *Ficus microcarpa* correlate greatly with their leaf size. Generally, it is proposed that the plant species having leaves of large surface area, short petiole, hard branch and sunken vein can retain higher amounts of PM/dust.

The physiological and metabolic processes inside the plants as well as the physical characteristics such as surface roughness and thickness vary greatly for young and old leaves. Usually young plants are capable to accumulate more foliar metal compared to mature or old plants. Bondada et al. [34] showed that the young fronds with immature sori absorbed about 69% more As compared to old fronds under foliar As treatment. This is because of the well-known fact that foliar absorption of heavy metals reduces with leaf maturity [182]. In fact, in new leaves, the cuticles are comparatively thinner, thereby more permeability for metal penetration. Moreover, the thickness of epicuticular wax, which is primary barrier against foliar metal transfer, is less in young leaves than old leaves [34]. Kinnersley and Scott [142] showed that the oldest tissues of plant foliar parts are generally more efficient in retaining heavy metals compared to younger leaves or stems. Some authors reported that before shedding, metals are remobilized to non-senescent plant parts, thus higher accumulation of metals in young leaves compared to mature leaves. This can be a possible reason of higher metal contents in young leaves compared to old leaves, as reported in *Tilia Europoea* [183] and *Aesculus hippocastanum* [184]. Moreover, redistribution of metals in plant after foliar uptake is generally an indication of phloem transport [185]. It is reported that phloem stream provide nutrients to young and new leaves, while xylem stream transfer nutrients to old and fully developed leaves.

The positions or orientation of trees regarding PM sources (industrial units and traffic) also affect the amount of metals deposited and adsorbed on plant leaves. Especially, mature plant leaves showed a clear correlation between metal depositions of Pb, Zn, Ba and Mn, and the distance from the traffic source. This also highlights the capability of atmospheric heavy metals to scatter over tens of metres from the source of emission [186]. Various previous studies evaluated the efficiency of different plant species for capturing and retaining PM with respect to leaf size and features [157,187]. From another side, dilution of metals with plant growth can decrease the total metal concentration in plants with their age.

The cuticle of plant leaves acts as an effective barrier against the uptake of foliar deposited metals. The composition and structure of the plant leaf surface therefore significantly affect the foliar transfer of heavy metals. Generally, the plant cuticle is an extra-cellular coating made up of biopolymer matrix with waxes embedded into the surface or deposited onto it [188]. The cuticle matrix generally comprised of bio-polyester cutin developing a web of cross-esterified hydroxyl. The structural composition of the bio-polymer matrix varies with the plant genotypes, species and organ, as well as the growing conditions and stage of development [144]. Different proportions of cutan and cutin have been reported in cuticular membranes of some plant species such as *Currants*, *Capsicum*, *Agave americana* and *Malus domestica* [189,190].

In addition to above mentioned characteristics of plants, some researchers evaluated the correlation between PM_{10} concentration and biomagnetic signals [191,192] or correlation between the amount of heavy metals in adsorbed atmospheric PM and the leaf magnetic parameters [192,193]. Nowadays, the role of leaf magnetic parameters towards heavy metal adsorption at leaf surface is well established. A strong correlation between Fe contents in the PM_{10} fraction and Fe concentration of plant leaves has been reported by Rai et al. [193]. Recently, Norouzi et al. [32] evaluated the correlation between the amount of heavy metals in adsorbed atmospheric PM and the leaf magnetic parameters at 21 different sites in Isfahan-Iran. It was observed that the magnetic susceptibility of leaves of *Platanus orientalis* increased in unwashed leaves due to the deposition of magnetic particles and heavy metals on leaf surfaces during the entire plant growth cycle. They reported that washing of *Platanus orientalis* leaves due to rainfall can reduce magnetic susceptibility and thereby deposition of heavy metals on leaf surface. They observed a linear correlation between leaf magnetic susceptibility values and heavy metals (Pb, Fe, Cu, and Zn) content in atmospheric dust.

6.3. *Effect of meteorological conditions on foliar uptake of heavy metals*

The climatic conditions greatly alter the potential of foliar metal uptake through their direct effect on the physico-chemical properties of plant and the leaf surface. The climatic conditions also influence the biological and metabolic processes inside the plant and in turns affect foliar transfer and compartmentation of metals. The immediate climatic conditions such as humidity, temperature and light at the time of foliar deposition influence plant metabolic processes and thereby influence penetration processes across the leaf surface and movement inside leaf spaces. Similarly, the environmental conditions in which plants are cultured and exposed to foliar heavy metals can alter metal penetration through their effects on leaf surface characteristics, effect on plant physiology and morphology as well as the composition and size of the canopy.

Relative humidity is another important climatic factor affecting foliar uptake of heavy metals. In fact, relative humidity influences the permeability potential of the plant leaf surface. Moreover, relative humidity greatly affects the physico-chemical responses of plants to adsorbed PM in terms of solubility or redox. At high relative humidity, permeability potential of the plant leaf surface may be enhanced due to hydration of cuticle. Similarly, the deposited PM and heavy metals remained wet under high relative humidity, which favours heavy metal penetration inside plant leaves. This is because under high relative humidity in the phyllosphere, heavy metals will theoretically remain as solutes and duration of their leaf penetration will be prolonged. Bondada et al. [34] reported that foliar absorption of As was 18% more for afternoon (12:00h–14:00 h) and night (20:00h–22:00 h) over the morning applications (08:00h–10:00 h).

Relative humidity can also enhance penetration of hydrated ions into the leaves by decreasing the hydrophobic potential of the cuticle surface. Several previous studies reported that high humidity enhances foliar metal uptake exposed to atmospheric PM [194]. Under high relative humidity conditions, heavy metal penetration can be high due to (i) delayed drying of droplets, (ii) swelling of cuticle, (iii) prolonged hydration of leaf deposits, and (iv) redissolution of salt deposits [49]. Prasad and Hagemeyer [194] also proposed similar findings and showed that high temperature and low rel-

ative humidity levels cause closure of stomata and shrinkage of plant cuticles, thereby inhibiting metal entrance into leaves. The penetration of foliar-deposited heavy metals through the cuticle is generally the highest under high relative humidity conditions. This is because of the fact that under high relative humidity conditions, the cuticle is in its most swollen and opened condition and vice versa [195].

Rainfall is another meteorological factor influencing metal deposition on plants and on their foliar uptake. Schreck et al. [25] showed that penetration and accumulation of foliar-applied Pb in the *Lactuca sativa* shoots was greatly correlated (correlation coefficient: 0.83) with the rainfall measurements. They reported that Pb accumulation in the *Lactuca sativa* shoots was the highest during the first and last weeks of Pb application due to the higher rainfall during these periods. Lawson and Mason [196] reported that Pb penetration and accumulation during rainfall were equal to or greater than dried deposition, thus proposing an increased Pb deposition and penetration during rainy period. In fact, during rainy periods, the stomatal openings and cuticles expansion favour high level of metal leaf penetration from the atmosphere [197].

7. Heavy metal behaviour inside plants after foliar uptake

7.1. Heavy metal translocation within plants after foliar uptake of heavy metals

The translocation factor (movement of metals within plants after foliar uptake) is a key parameter for sanitary risk assessment studies. After penetration through leaves, the translocation of metals within plants occurs via penetration through the cuticle [145]. However, quantitative values largely depend on the environmental conditions and characteristics of metal and plant. Other key factors influencing heavy metal translocation inside plants after foliar penetration include type of PM and heavy metal deposited on the leaf surface, plant maturity and cuticle composition. After foliar penetration, heavy metals are transported to other plant parts via phloem vascular system in the same way as photosynthates. This active metal transport inside plants is largely dependent on plant metabolism.

Additionally, the physiological behaviour of the metals and the stage of plant development are also important factors. Thus, heavy metal contamination of edible plant parts depends on the growth stage at which the plant is exposed to atmospheric PM. The flowering growth stage is considered as a critical stage for numerous metals and plants [198]. Flowering stage corresponds to a maximum demand of certain nutrients in different metabolic processes. Although, there is no or very little demand of non-essential elements, but these elements follow the same trend of analogues essential elements. However, there exists very rare data regarding the effect of different growth stages and metabolic processes on metal translocation dynamics inside plants.

There is lack of data regarding metal movement/translocation inside plants. It is proposed that foliar-applied metals penetrate the cuticle into the leaf free space from where they may undergo selective phloem loading stage [199] followed by long-distance transport inside the plants. This movement inside plants varies with the chemistry of heavy metals. For example, immobile metals such as Pb may precipitate as the phosphate [200] and displays resemblances to Ca in this regard. Dollard [201] reported no or very little transportation of foliar applied Pb into the seeds and pods of the *Phaseolus vulgaris*. Therefore, it is believed that heavy metal accumulation by foliar transfer is of similar importance to the root transfer only for exposed organs (leaves) [202]. This is because of the fact that heavy metal level in roots, fruits, pods and other aerial organs appeared to be generally negligible after foliar translocation.

Moreover, binding of metals with ionogenic sites on the cell walls may also restrict their movement inside plant leaves. For example, Pb has high binding affinity for cellulose in plant cells [203]. Similarly, specific binding sites have been reported for Cu, Zn and Mn in *Saccharum officinarum* leaf tissue [204]. However, immobile metals transport inside plants by several pathways. Firstly, immobile metals can move inside plants with the bulk flow of metabolites when the levels of metals are sufficiently low so that their solubility products are not surpassed. Secondly, immobile metals may form chelates or complexes with organic compounds present in the phloem, which inhibit their precipitation.

Some studies in late 20th century reported transport of heavy metals especially Pb after foliar uptake. Dollard [201] used radioactive tracer ^{210}Pb to evaluate the foliar uptake and compartmentation of Pb in *Raphanus sativus*, *Daucus carota* and *Vicia faba* under glasshouse conditions for periods. He observed that the amount of the foliar-applied Pb actually transported to the root tissues was 0.1%, 0.1–0.3% and <1%, respectively, in *Raphanus sativus, Daucus carota* and *Vicia faba*. Tso and Fisenne [205] reported that a small proportion (0.1%) of foliar-applied ^{210}Pb was detected in root tissues of *Nicotiana* plants, which was linked to soil contamination in which the plants were cultivated. They proposed that foliar-applied Pb was mainly retained on the leaf surface for a period of 2-weeks.

Similar findings were reported by Athalye and Mistry [206], who observed no indication of Pb movement through the cuticle of *Vicia faba* plants. Using autoradiographs, Hemphill and Rule [207] showed slight translocation of foliar-applied ^{210}Pb from the leaves of *Raphanus sativus* and *Lactuca sativa* towards roots (approximately 0–08% in *Raphanus sativus* and 0.01 in *Lactuca sativa*). Similarly, Pb movement from leaf towards roots in *Hordeum vulgar* plants was reported by Aakrog [208]. They proposed that Pb contents in the grain could be due to atmospheric Pb pollution.

7.2. Heavy metal speciation within plants after foliar uptake of heavy metals

The knowledge of heavy metal speciation inside the plant system is indispensable as it provides key information regarding heavy metal detoxification and homeostasis mechanisms. Nowadays, it is well-known that heavy metal speciation governs their biochemical behaviour (compartmentation, toxicity and detoxification) inside plants [91,209]. Majority of the studies dealing with heavy metal speciation reported that total amount of metals is not a good indices of their compartmentation, toxicity and detoxification inside plants. It is reported that metals undergo changes in speciation after foliar uptake. Published data on metal speciation in plants mostly concerns root exposure experiments [210]. However, there is actually very little data available regarding heavy metal speciation in plants after foliar uptake. The changes in metal speciation after foliar application can be due to transformations occurring after contact with the leaf. Various hypotheses are as follows: (i) changes of humidity and temperature transform PM at the leaf surface and (ii) the changes due to phyllosphere activity [18,211]. The changes in metal speciation inside the plants after foliar uptake could also result from the interaction with biochemical compounds present in the phyllosphere [212]. These findings suggest that metal speciation in plants depends on exposure conditions and phyllosphere conditions. As suggested by Gandois et al. [213] and Eichert and Goldbach [214], metal speciation and concentrations in plant leaves could be altered by interactions between microbes and PM on the phyllosphere.

Metal speciation inside plants after foliar exposure greatly differs by plant species. Schreck et al. [93] reported that in *Lactuca sativa*, Pb speciation in leaves after foliar exposure (determined by X-ray absorption spectroscopy (XAS)) was significantly different

both from Pb speciation in pristine and rye-grass. They reported that in *Lactuca sativa*, original minerals (PbO and $PbSO_4$) were the major species, but in rye-grass, Pb–organic species were observed in majority. Observations performed on *Lactuca sativa* exposed to Pb-rich fallout showed (i) fine Pb and Fe-rich particles on stomata ($PbSO_4$, PbO, $PbCO_3$ and Fe_2O_3), (ii) secondary species, such as needle crystals, enriched in Pb due to transformation at the leaf surface and (iii) the presence of primary PM (with $PbSO_4$ and $PbCO_3$ as major species) under an organic layer [18]. Similarly, *Petroselinum crispum* leaves were observed by μXRF and SEM-EDX after foliar Pb application. Aggregates of particles <1 μm were observed on the surface. Other Pb-containing particles were enriched in Fe and Mn, Ca and K, which may correspond to ultrafine particle aggregation.

Changes in metal species inside plants after foliar uptake also depend on metal type. For example, in case of As, the form of As after uptake in the frond of *Pityrogramma calomelanos* var. *austroamericana* was mainly arsenite (As(III)) regardless of the applied form (arsenate As(V)) [215]. In case of Pb, there was transformation from inorganic to organic form depending on plant type. Some studies showed that foliar application of two inorganic Se species were metabolised by the plant to form two major organic Se species [216,217].

7.3. Heavy metal toxicity to plants after foliar uptake of heavy metals

The toxicity of foliar absorbed heavy metals is not well-established. There exists complex variation regarding the effect of foliar absorbed heavy metals on plant toxicity. For example, Kovácik et al. [218] reported that foliar application of Ni + Cd to *Tillandsia albida* caused significant decrease in water contents, reducing sugars, chlorophyll a, chlorophyll *b* and carotenoids. Moreover, N metabolism and total phenol contents were strongly affected by the Ni + Cd. However, there was no effect of Ni and Cd to *Tillandsia albida* when these metals were applied alone [218]. Mineral nutrients (Ca, K, Mg, Na, Zn and Fe) were not affected by foliar application of Cd and Ni [218].

Al-Subu et al. [219] showed toxicity to *Vicia faba*, *Daucus carota*, *Raphanus sativus and Cucurbita pepo* vegetables after combined foliar application of Cd, Pb and Cu. Ugolini et al. [220] also reported that no significant correlation was found between metal concentrations and biomass indices, after foliar uptake of heavy metals. They reported that only leaf dry mass content was affected by foliar metal accumulation. Similar results of non-significant effects of foliar Ni application on growth of *Solanum lycopersicum* were also reported by Shimada and Ando [221]. In contrast, Hosseini and Khoshgoftarmanesh [222] reported that foliar application of Ni significantly increased fresh weight of *Lactuca sativa*. They also reported that the effect of foliar Ni application on fresh weight varied with Ni applied source (urea-Ni and $NiCl_2$) and *Lactuca sativa* cultivar (Concoistador cultivar and Grizzly cultivar). Recently, some studies [223,224] also reported increase in fresh weight of plants after foliar Ni application. However, there is no clear relationship between foliar metal uptake and toxicity.

Recently, Hong et al. [225] reported that foliar application of Ce and Cu to three week-old *Cucumis sativus* seedlings showed a decrease in transpiration rate (11% and 17%) and net photosynthesis rate (22% and 30%), respectively, compared with control. Both the metals considerably decreased fruit firmness, compared to control. Similarly, some authors reported beneficial effects of foliar applied metals (essential metals such as Zn, Cu and Mg) on plant growth and development [226]. For example, an increase in grain yield and grain Zn concentration in *Phaseolus vulgaris* has been reported under foliar Zn application [28].

Reactive oxygen species (ROS) are unavoidable and natural by-products of aerobic processes taking place in living organisms. Plants are known to produce ROS naturally in various organelles such as chloroplasts, mitochondria and peroxisomes [227]. These radicles are usually chemically very reactive, unstable and short lived. These species contain unpaired electrons in their valence shell. These ROS include: hydrogen peroxide (H_2O_2), singlet oxygen ($^1O_2$), superoxide anion ($O_2^{\bullet -}$), hydroxyl ($HO^{\bullet}$), alkoxyl ($RO^{\bullet}$), peroxyl ($RO_2^{\bullet}$) radicals, organic hydroperoxide (ROOH). Enhanced production of ROS is usually the result of heavy metal toxicity in plant tissues [228,229]. Overproduction of ROS inside plants is generally considered a negative stress-induced factor, but these free radicles also act as messengers involved in signal transduction pathways [151].

Plant exposure to heavy metals causes an imbalance between ROS production and elimination, resulting in dramatic physiological changes known as "oxidative stress" [230]. Heavy metal-induced enhanced production of ROS may eventually lead to cell death due to oxidative stresses such as membrane lipid peroxidation, damage to RNA and DNA, inhibition of key enzymes and protein oxidation [227,229]. Kovácik et al. [218] reported that foliar application of Cd alone and in combination with Ni to *Tillandsia albida* significantly enhanced H_2O_2 production. Decrease in GSH and increase in GSSG confirms oxidative stress under Ni + Cd foliar application to *Tillandsia albida*. However, application of Ni alone has no effect on H_2O_2 production. Similarly, despite increased *Tillandsia albida* production of ROS, lipid peroxidation was not observed under Ni and Cd foliar application in *Tillandsia albida*. This showed that foliar application of metals may or may not cause oxidative stress depending on the type of metal and plant.

7.4. Plant defense mechanisms after foliar uptake of heavy metals

Once heavy metals have entered the cell, a plant uses various tolerance/defence mechanisms by which they can cope with metals toxicity. Plant tolerance to a specific heavy metal is controlled by an inter-related network of molecular and physiological mechanisms. Different plant species may differ in their strategy to tolerate excess heavy metals.

There may exist more than one tolerance mechanism within the one plant species. Plants have evolved both adaptive and constitutive mechanisms to cope with high levels of exposed heavy metals [231]. These mechanisms include reduced metal uptake and transport, induction of specific heavy metal transporters, limiting accumulation in sensitive tissue or sequestration in tolerant organs (vacuoles), stimulation of processes controlling the toxic effects of ROS (antioxidative enzymes), production of stress proteins, and synthesis of signalling molecules such as nitric oxide and salicylic acid. These tolerance and or adaptation mechanisms assist plants to alleviate the damage induced by oxidative stress and to maintain their cellular redox state [232,233]. Very little data is available regarding the activation of defence mechanism after foliar metal uptake. Moreover, what specific plant defence mechanism is active, and at what efficiency, is not well clear for foliar metal uptake.

One of the defence mechanism adopted by plants is the "avoidance" when plant species can limit metal uptake. Avoidance mechanism involves reduced absorption of toxic metals by reduced uptake, biosorption to cell walls and extracellular precipitation. Physico-chemical characteristics of leave surface play an important role in limiting the absorption of heavy metals into leaf cells. Indeed, the plant aerial surfaces are endowed with a diverse and complex array of specialized physical and chemical adaptations that act as plant tolerance to various conditions such as extreme temperatures, rain, pollutants, physical damage, unfavorable irradiation, deficits of vapor pressure, pathogens and insects.

The surfaces of aerial plant tissues are also well-adapted to govern exchange of gases and water vapor, and to limit the losses of metabolites, nutrients and water under harsh environmental con-

ditions. These features of aerial plant surfaces also help plants to control foliar absorption of metals and other pollutants. Several studies reported retention of heavy metals on leaf surface resulting in decreased foliar uptake of heavy metals to plants. Some researchers consider it a defence mechanism adopted by plants against external stresses.

In addition to "avoidance", plants cope with heavy metal stress through "tolerance". A strong sink to store toxic metals without toxicity is critical for their homeostasis under high heavy metal levels inside plants [229,234]. In this way, plants can avoid heavy metal-induced toxicity to different cellular compounds. Since the plant leaves are key photosynthetic organs, it is vital that foliar-absorbed metals and other nutrients or chemicals sustain the integrity of the leaf both at ultrastructural and organ level. Sequestration of metals in tolerant organs is supposed to be an important aspect in plant metal tolerance and detoxification [36].

The plants have ability to bind and sequester metals to molecules (such as vacuoles) in order to inhibit their harmful effects. Bondada et al. [34] observed that under foliar As application, large amounts of As(up to several hundred ppm) was sequestered into sori. This enhanced accumulation of As in sori is probably a tolerance strategy adopted by fern [3]. At molecular level, heavy metals are generally transported and sequestered into the vacuoles, thereby eliminating these metals from the sensitive cellular compartments where metabolic reactions takes place [227]. Heavy metals detoxification in aerial parts of plants occurs by their binding with ligands and/or moving them into vacuoles [235].

Vacuolar compartmentalization of heavy metals is an efficient detoxification strategy by constricting them into the limited site where these harmful metals have no excess to sensitive metabolic reactions and the safety is ensured. Recently, a range of gene families has been identified that play key role in heavy metal uptake into cells, xylem loading, vacuolar sequestration and remobilization from the vacuole. These transporter families include cation diffusion facilitators (CDF), natural resistance-associated macrophage (NRAMP), ZIP (ZRT, IRT-like protein), heavy metal ATPases (HMAs), ATP-binding cassettes (ABC) and cation exchangers (CAXs) [235–237]. Among these, ABC, NRAMP and CDF have been recognized as major heavy metal tolerance transporters [238]. However, very little is known regarding the role of these gene families in heavy metal vacuolar sequestration under foliar application. In As hyperaccumulator plants, arsenate reductase enzyme reduces As(V) to As(III), which is then complexed with free thiol groups followed by storage of the arsenite-thiolate complex in vacuole [215].

Inside plants, ROS are scavenged by a complex system of both non-enzymatic and enzymatic antioxidative system. Among non-enzymatic antioxidants, cysteine, metallothioneins, phytochelatin and glutathione are well-known for their role to bind/chelate heavy metals and/or scavenge ROS inside plant cells. Therefore, these proteins/ligands are involved in heavy metal detoxification and homeostasis [227,229]. These proteins/ligands are the best categorized metal-binding compounds in plant cells. These metal-binding compounds belong to various classes of cysteine-rich protein molecules and play key role in heavy metal detoxification in plants. Sytar et al. [239] reported that foliar application of Ni (0, 0.5, 1.0, 3.0, and 5.0 mM) in *Fagopyrum esculentum* enhanced MDA and total phenolic contents after 24 h of Ni treatments. Foliar Ni application enhanced caffeic acids, *p*-hydroxybenzoic, chlorogenic and hesperetic contents after 24 and 48 h in *Fagopyrum esculentum* [239].

Activation of antioxidative enzymes is an intrinsic defense strategy to control ROS contents according to the metabolic needs of cells at a specific time. These antioxidants include the enzymes glutathione peroxidase (GPX), glutathione S-transferase (GST), glutathione reductase (GR), dehydroascorbate reductase (DHAR), ascorbate peroxidase (APX), superoxide dismutase (SOD) and catalase (CAT) [227,240–242]. Activation of these enzymes under heavy metal stress is well-known and is reported in various plant species [227]. These enzymes act in conjugation with each other to scavenge excess ROS. Among these enzymes, CAT which is generally present in peroxisomes and mitochondria, decomposes H_2O_2 by an energy efficient mechanism [243]. Superoxide dismutase dismutates two $O_2^{\bullet}-$radicals to O_2 and H_2O_2, and thereby controls steady state level of $O_2^{\bullet}-$in plant cells. GPXs detoxify H_2O_2 in plants as well as phospholipid hydroperoxides and lipid [243].

GST enzymes catalyze the conjugation of reduced GSH to xenobiotic substrates during detoxification. GST contains six functional classes in the plants: DHARs, phi, theta, tau, zeta and lambda [227]. APX and two molecules of ascorbate catalyse the reduction of H_2O_2 into H_2O. GR is involved in maintaining GSH level in plant cells [243]. However, the activation of antioxidant enzymes under foliar applied heavy metal stress is not well known. Kovácik et al. [218] reported that foliar application of Cd increased activities of APX, SOD and GPX in *Tillandsia albida*. Moreover, significant increase in H_2O_2 production as well as reduced and oxidised glutathione contents showed occurrence of oxidative stress in *Tillandsia albida* under Cd + Ni foliar application. However, phenolic enzymes, soluble proteins and free amino acids showed negligible responses to (Cd + Ni) foliar application. Enhanced activity of antioxidant enzymes in Cd-treated *Tillandsia albida* suggests that heavy metal homeostasis in these plants might be linked with the activation of enzymes.

8. Comparisons of foliar and root heavy metal uptake by plants

As stated above, metals can accumulate in plants both through root [151] and/or foliar uptake [25,244] (Fig. 4). The soil–root transfer of metals is the major pathway by which heavy metals enter the plants. However, only few studies compared the influence of the two ways of metal uptake by plants [35]. The mechanisms of metal uptake, translocation, compartmentation, toxicity and detoxification differ greatly with applied metal pathways [143,245]. It is very difficult to differentiate that metal concentration within internal plant tissues either is taken up by root cells from the soil or by leaf surfaces from atmosphere, because the two kinds of uptake pathways can occur simultaneously near urban and industrial areas.

There exist very old and rare data which have separated the foliar accumulation from root uptake [95,246,247]. Kozlov et al. [115] reported that there was a significant variation in annual foliar levels of heavy metals in *Salix*. They reported that this variation is difficult to explain if soil-root transfer of heavy metals is the major source. However, foliar heavy metal absorption can explain these variations to a great extent by taking into account the variation in weather conditions that contribute greatly towards foliar metal deposition.

Schreck et al. [248] performed two separate experiments to evaluate and differentiate between foliar and root metal transfers. For the root metal transfer experiment, lettuces and rye-grass were cultivated in earthen pots containing Pb contaminated soil (2000 mg kg^{-1}). For the foliar transfer experiment, pots containing lettuces and rye-grass were placed near a smelter. A geotextile membrane was placed on the top of the soil to protect it from atmospheric fallouts and thus to avoid soil contamination and metal transfer via root pathway. They reported considerable Pb accumulation via root (36 mg/kg in lettuces and 82 mg/kg in rye-grass) and shoot transfer (171 mg/kg in lettuces and 700 mg/kg in rye-grass).

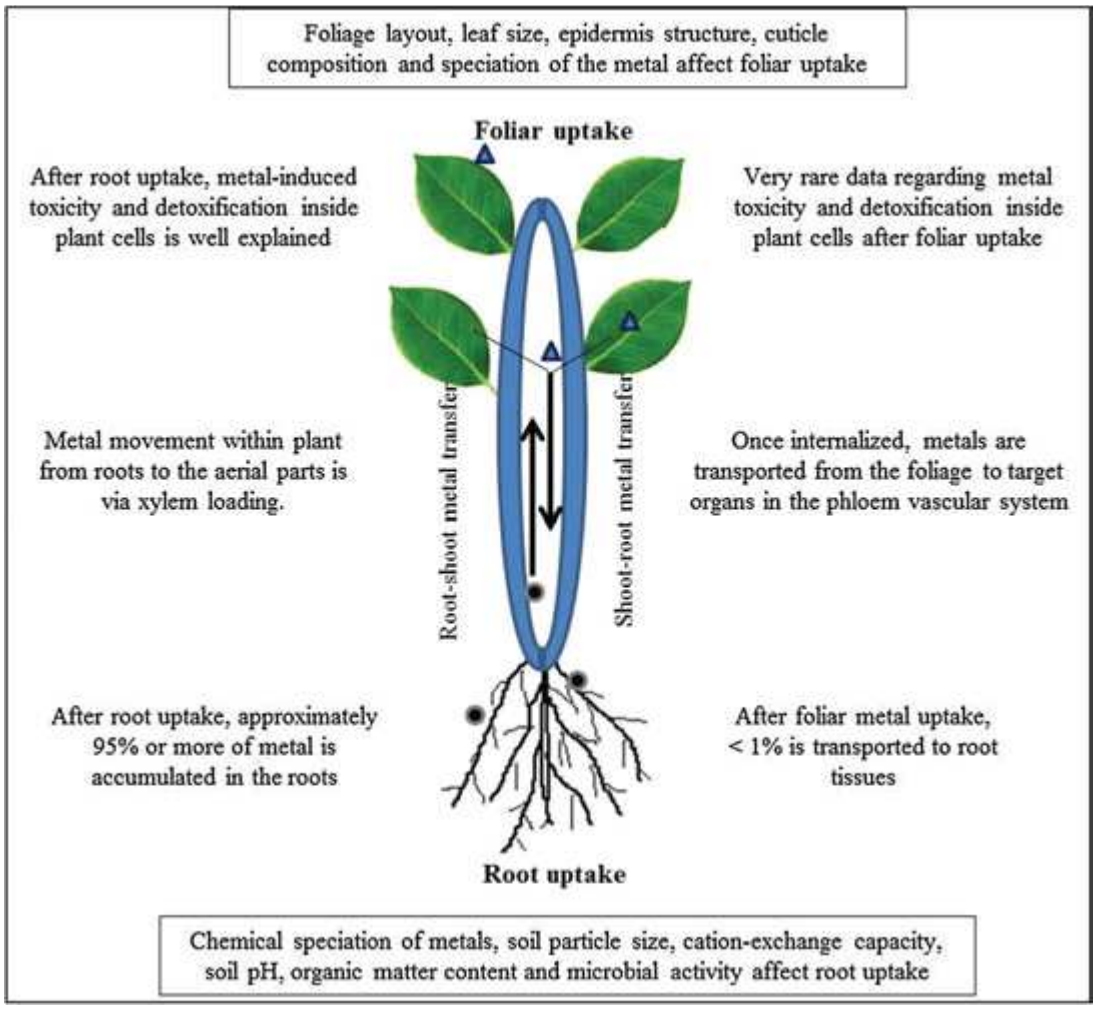

Fig. 4. Comparison of foliar and root metal uptake.

8.1. Comparison of heavy metal entrance to plants by foliar and root pathway

For root metal uptake, generally the part of metal found in the soil solution is first adsorbed onto the root surfaces, followed by their binding to polysaccharides of the rhizodermal cell surface or carboxyl groups of mucilage uronic acid [249]. After adsorption on roots surface, heavy metals penetrate the roots passively and diffuse through translocating water streams. In the case of foliar transfer, PM may be adsorbed on the leaf surface of plants due to wax cover and leaf hairs [250], depending on their size [25,146]. Based on phobicity of pollutants, two pathways of foliar metal uptake have been anticipated; diffusion through the cuticle for lipophilic elements and via aqueous pores of the stomata and cuticle for hydrophilic compounds [153] (Fig. 1).

8.2. Comparison of factors affecting heavy metal uptake by foliar and root pathway

Different factors affect metal uptake and accumulation index by plants under root and foliar metal uptake. Root metal uptake by plants varies with soil and plant type, chemical speciation of metals in soils, soil particle size, cation-exchange capacity, soil pH, organic matter content and microbial activity. In contrast, foliar metal uptake depends on several physical, chemical and biological factors [142]. Physical factors include the type and chemistry of heavy metals as well as the characteristics of plant leaf surface. Chemical factors take into account the speciation of metals and cuticle composition [145]. Biological factors concern the growth stage at which heavy metals get deposited on plant surface [251].

8.3. Comparison of heavy metal transport after foliar and root pathway

Metal movement within plant from roots to the aerial parts is via xylem loading, which is assisted by unidentified transport processes, and occurs via symplastic or apoplastic transport [36]. Metals are transported with different chelates [252], and the transportation is generally governed by transpiration [36]. A number of important membrane transporter gene families have been recognized and categorized in recent years responsible for metal transportation to aerial parts of plants [232]. In contrast, there is no clear evidence regarding the role of different chelates and transporter genes in metal transportation inside plants after foliar uptake. The process of metal translocation within plants after foliar uptake take place via penetration through the cuticlar layer, desorption in the apoplast and binding to the subjacent mesophyll cells [145]. After foliar absorption, heavy metals are transported inside the plants from aerial parts towards different plant organs (roots, flowers fruits etc.) via phloem stream similar to the photosynthates.

8.4. Comparison of heavy metal compartmentalization after foliar and root pathway

The type of exposure (shoot or root) may have different effects on metal compartmentalization (distribution at the tissue and cellular scale) in plants [143,253] and consequently metal bioavailability and toxicity. In case of heavy metal uptake by plant roots, the major portion of absorbed metals especially Pb (about 95% or even more) is sequestered in the root cells, with a limited translocation to aerial tissues unless the plant is chelates-assisted or hyperaccumulator [209,254,255] or microbial assisted [256]. The restricted translocation of heavy metals to aerial plant tissues is due to the presence of physical barrier (Casparian strip) in plant roots [36], precipitation intercellular space as insoluble metal-salts [257], or sequestration in the vacuoles of cortical or rhizodermal cells [258]. In case of foliar metal uptake, majority of the absorbed metal is stored in leaf tissues with a small portion (<1%) transported to root tissues [201,259]. Leaf parenchyma contains major part of foliar applied metals [115]. Observations performed on *Lactuca sativa* exposed to Pb-rich fallout showed Pb particles on stomata, at the leaf surface, and under an organic layer of leaves [18]. So far no study reported decreased transportation of metals from shoot to roots.

8.5. Comparison of heavy metal speciation after foliar and root pathway

The type of exposure (root or shoot) may have different impacts on metal speciation in plants [143,253] and consequently metal bioavailability and toxicity. Heavy metals form chelates or complexes with organic amino acids [260] while passing through the xylem. However, Pb may also be transferred, in inorganic form, as is Cd [36]. The association of Pb with cell wall components was previously observed by EXAFS as the main Pb storage mechanism in the leaves of both accumulator and non-accumulator ecotypes of *Sedum alfredii* after Pb root exposure [261]. The formation of pyromorphite was observed by EXAFS in the leaves of *Phaseolus vulgaris* after Pb root exposure [253]. The presence of Pb–organic acid complexes might be interpreted as Pb sequestration in vacuoles, as previously observed for Zn, Ni, and Cd in various plant species [253,262]. However, after foliar exposure, majority of Pb–organic species (Pb bound to polysaccharides of the cell wall and Pb–organic acids) were observed. Thus, Pb-rich particles deposited on *Lolium* leaf surfaces likely underwent dissolution followed by the transfer of Pb inside the leaf tissue. As suggested by Gandois et al. [213] and Eichert and Goldbach [146], metal speciation and concentrations in leaves could be modified by interactions between PM and microbes on the phyllosphere.

The variation in metal speciation under foliar and root uptake can be due to variation in rhizosphere and/or the phyllosphere zones as well as mode transportation of metals inside plants [263,264]. The rhizosphere hosts an intense microbial activity and is a place of excretion of various inorganic and organic compounds [256,265–267]. Thus, these mechanisms involved in the rhizosphere and/or the phyllosphere zones could be effectively responsible for the observed metal speciation and compartmentalization changes as a function of the plant species (as, for instance, the nature and quantities of root and foliar exudates depend on the plant considered). In addition, after its plant uptake, the metal may undergo biotransformation in the plant directly in relation to the plant species and certainly as a function of the pathway of transfer. The pathway and mechanisms of metal transfer within plants differ in the rhizosphere in comparison with the phyllosphere. In the case of root exposure, the influence of the rhizosphere activity on the status of metals or metalloids in the substrate has been evidenced in many studies [209,266]. After root uptake, metals are transferred by the apoplasmic pathway or symplastic transport across the root cortex to plant storage tissues. While passing through xylem sap, metals could forms complexes with amino acids like histidine, organic acids as citric acid, fumaric and malic acid [268] or phytochelatins [227]. However, metals may also be transferred in inorganic form like Pb and Cd [269]. In case of foliar uptake, metals may or may not undergo changes in speciation. Changes in metal speciation after foliar uptake can be due to changes of humidity and temperature at the leaf surface and the changes due to phyllosphere activity [18,211]. Uzu et al. [270] reported that the speciation of Pb varied after interaction with plant leaves. Similarly, Shahid et al. [271] reported that the popular leaves contaminated with heavy metals, near a smelter, fell on soil; thereby added heavy metals into surrounding soil. These authors reported that the speciation of heavy metals added to soil via fall of leaves varied considerably compared to the speciation of heavy metals which have directly fallen on soil.

Comparison of heavy metal toxicity after foliar and root pathway: toxic effects of heavy metals vary with the mode of entrance to plants, i.e., via roots or foliar. It has been shown that specific applied levels of heavy metals can influence plants differently depending on what part/organ of the plant is directly exposed to the metals. Bernal et al. [272] showed that Cu supplementation via roots or leaves pathway showed different effects to soybean plants. After root uptake, metals have capacity to decrease seed germination and root elongation, reduce plant biomass, and inhibit chlorophyll biosynthesis [7,36,151]. While inside a cell, metals affect respiration, photosynthesis, nutrient balance and enzymatic reactions as well as various other physiological parameters [210,227,231,273]. Exposure to heavy metals also induces over production of ROS in plants, which seriously disrupts the redox status of cells [210,229,240,274]. However, foliar application of heavy metal also induces a wide range of toxic effects to different metabolic and physiological processes inside plants [25,275], but the extent of toxicity is generally less compared to root metal uptake. Some studies even reported no effect of positive effects of foliar metal uptake. For example Cu foliar application increased photosynthetic activity and chlorophyll content [272,276].

Comparison of heavy metal toxicity after foliar and root pathway: under heavy metal stress conditions, plants employ a number of strategies to survive the toxic effects of metals. Under root metal uptake, several studies showed that plants tolerate high levels of heavy metals by chelating through the synthesis of organic and amino acids, GSH, or heavy metal binding compounds such as PCs and MTs, sequestration within vacuoles, and activation of the antioxidant enzymes [36,229]. However, very little data is available regarding the activation of defence mechanism after foliar metal uptake. Recently, overproduction of ROS, decrease in GSH and increase in GSSG contents as well as significant increase in the activities of antioxidative enzymes (APX, SOD and GPX) has been reported in *Tillandsia albida* under (Cd + Ni) foliar application. However, lipid peroxidation remained unaffected under Cd + Ni foliar application. This showed that foliar metal application may result in ROS production and activation of defense mechanism. Gawel et al. [277] showed that PCs are bioindicators of atmospheric metal pollution exposure via foliar uptake. However, what specific plant defence mechanism is active, and at what efficiency, is not well clear for foliar metal uptake.

Perspectives of comparison of heavy metal uptake by foliar and root pathway: the above mentioned differences between soil-root pathway and atmosphere-leaf pathway with respect to uptake, speciation, transportation, compartmentation, toxicity and detoxification raise questions as whether these differences are due to variations among plants or in response to a more general phenomenon. Uptake of heavy metals by plants (whether root or shoot) is a complex phenomenon, and involves various steps. The dissimi-

lar plant responses observed in response to these two metal transfer pathways might be rationalized presuming different metal uptake and tolerance strategies in root and leaf cells. Therefore, a lot need to be explored in the context of foliar metal uptake.

9. Health risk assessment of heavy metal after foliar uptake

Estimating the level of exposure of heavy metals and tracing their routes of contamination to the target organisms are critical for understanding the health risks involved [1]. Health risks related with atmospheric contaminations may arise primarily from inhalation of particles and also consumption of polluted food [54]. It is well mentioned above that the mechanisms of metal uptake, translocation, compartmentation, toxicity and detoxification differ greatly with applied metal pathways, which in turn may affect metal accumulation in edible plant parts and hence the potential risk associated. Therefore, it is necessary to evaluate the risk assessment of foliar deposited heavy metals. Heavy metal level in edible plant parts after foliar transfer can be used to estimate the potential health risk assessment such as, estimated daily intake (EDI), hazard index (HI), tolerable daily intake (TDI), hazard quotient (HQ) and carcinogenic risk (CR) [31]. These health risks parameters are compared with standard toxic values or oral reference dose (RfD), which represent an estimated daily exposure of human body to the metal that has no hazardous effect during life time [278]. The Rfd values for Cd, Pb, Ni, Cr, Cu, Mn and Zn are 0.001, 0.004, 0.02, 1.5, 0.04, 0.033 and 0.30 (mg/kg body weight per day), respectively [278].

Several previous studies used these parameters to evaluate the potential toxicity of heavy metal polluted vegetables, but majority of the studies take into account root metal transfer [279,280]. Recently, Xiong et al. [54] evaluated EDI, HQ and HI of Cu, Cd and Pb in different vegetables (*Ipomoea aquatica Forssk, Allium fistulosum, Brassica juncea, Portulaca oleracea, Lactuca sativa, Cichorium endivia, and Amaranthus mangostanus*) after foliar application. They reported that the values HIs exceeded 1 in *Amaranthus mangostanus* (3.77), and also in *Ipomoea aquatica* (1.97) due to the high metal levels in leaves. Similarly, Xiong et al. [16] reported that high levels of Sb, Cd, Pb and Zn were observed in the leaves of *Spinacia oleracea* and *Brassica oleracea* after foliar application. They reported that TDI was higher for these metals compared to their threshold levels (0.15, 0.4 1.0, and 300 g kg^{-1} d^{-1} respectively for Sb, Pb, Cd, and Zn) [281,282] (Table 4). Schreck et al. [25] concluded that foliar uptake of heavy metals can cause significant health hazards when high levels of heavy metals are present in the air. Therefore, it is highly necessary to evaluate health risks associated with foliar uptake of heavy metals as a result of atmospheric deposition, especially in case of urban agriculture (kitchen gardening) [113].

In addition to toxic effects of metals in plants, food safety has gained considerable attention worldwide [283,284]. During last 2–3 decades, numerous studies focused on the health risks associated with the ingestion of contaminated vegetables [284–286]. It is reported that the metal contents in edible parts of vegetables may exceed the maximum permissible limits (MPLs) with serious public health implications [287]. Heavy metals can be highly harmful to the human even at low exposure level as there is no effective tolerance or excretion mechanism. Consumption of vegetables contaminated with heavy metals is considered responsible to a lesser or greater extent for various clinical conditions: intrauterine growth retardation, depletion of nutrients in the human body, disabilities with malnutrition, impaired psycho-social faculties, upper gastrointestinal cancer and immunological defenses [288]. Numerous previous studies evidenced the carcinogenic effects (chromosomal aberrations and mutations in cultured cells) of metals such as Cd, As, Pb etc. in humans. Similarly, clinical studies in industrial workers proved links between Cd exposure and human cancer of the kidney, lungs, bladder and prostate [289–291].

Besides potential human health risks associated with the consumption of heavy metals contaminated vegetable, presence of toxic metals in plant products (oil, herbal medicine feeds and foods) can also induce health risks. Earlier studies have proposed that some medicinal, aromatic and herbal plants can accumulate considerable amount of heavy metals in their plant parts, which are used for preparation of various products used by human [103,292–294]. Although the concentrations of heavy metal in plant products (oil, herbal medicine feeds and foods) are low, metals may accumulate in human due to continuous usage of these plant products. Essential oils have been employed widely as aromatic agents in pharmaceutical, perfumery, nutraceuticals industries, and cosmetic and functional food. The medicinal aromatic plants are most widely used to treat the different problems in human beings [295]. Ingestion of heavy metals even in a very small concentration can negatively affect various biochemical and physiological functions as well as survival of organism. However, there exist very rare data regarding foliar heavy metal accumulation in medicinal, aromatic and herbal plants as well as their products.

The effect and contents of heavy metals after foliar uptake on the quality and content of essential oils remains undiscovered. Certain studies have revealed that some of the aromatic plants could be grown safely (with low heavy metal contents) around smelters [296–298], but the foliar pathway aspect was not described in these studies. Moreover, essential oils have been reported to possess the antimicrobial activity and to contain significant quantity of antioxidants [299,300]. Nevertheless, no study has yet evaluated the effect of foliar metal transfer on antimicrobial activity of plants. Similarly, physiological attributes of medicinal, aromatic and herbal plants have not yet been explored.

Some studies reported management practices to avoid health risks associated with the consumption of heavy metal polluted vegetables. For example, Schreck et al. [301] reported that washing of vegetables with water can remove 25–29% of total Pb-rich particles. However, they reported that the total metal contents were still up to 400-times higher compared to control. Khalid [302] proposed that different vegetables accumulate different levels of metals in their edible plant parts. People eat a mixture of vegetables and crops, and not just one plant species. Therefore, choice of cultivated vegetable can be a good strategy to manage urban agriculture under high heavy metal foliar deposition and transfer. Similarly, metal accumulation by plants via root or foliar transfer varies greatly among different plant species. Therefore, plant species with low soil-plant metal transfer may be recommended for heavy metal polluted soils, while others with low atmosphere-plant metal transfer may be preferred for areas with high atmospheric deposition of heavy metals.

10. Management of contaminated plant residues

When heavy metal levels in the plant biomass exceed the MAL, plant biomass is considered to be a potentially hazardous material. Some authors proposed that plant species, containing high levels of heavy metals, may be disposed-off to minimize the associated health risks [303,304]. However, treatment, storage and placement of contaminated plant biomass are key secondary environmental contamination issues, which need to be addressed.

Few studies proposed a radical approach to address this disposal problem by incorporating a thermochemical conversion of contaminated plant material to energy followed by heavy metal recovery [305], which is considered as one of the most economical and safe approaches of utilizing the contaminated plant biomass. Gasification and combustion are important approaches used for producing

thermal and electric energies from contaminated plant biomass. Another operational method could be thermochemical processing of contaminated plant biomass on pyrolysis [306,307]. Similarly, ashing of contaminated plant biomass can produce bio-ores.

11. Modeling of air pollution to assess foliar uptake of metals

Despite considerable advancement during last few years, heavy metal atmospheric modeling remains an important area of research. Modeling of air pollutants is a numerical/mathematical tool generally used to estimate the relationship between emissions, meteorology, atmospheric concentrations, deposition, and other factors [308–310]. Computer models of air pollution provide a rapid and alternative approach to predict air pollution by heavy metals and other pollutants [310,311]. Estimation of air pollution gives vital, numerical data about ambient concentrations and deposition of heavy metals. However, pollution models can predict air quality/pollution at definite times and locations. Different researchers have used various strategies for estimating air pollution. These strategies include: (i) predicting direct quantification from monitoring sites, and (ii) analysis of point sources, such as industrial units or traffic intensity on roadways.

Air quality/pollution models are generally used to understand tropospheric dynamic and to estimate heavy metal levels in air in areas where no recording facility is available. Some of these models include Global/regional atmospheric heavy metals (GRAHM), Heavy Metals Eulerian Transport (HMET), Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) and Dynamic Estimation of Contaminant concentration using Attenuation factors (DECA). However, only few models are capable to estimate heavy metal levels in air. These models generally not directly relate to foliar deposition or absorption (the amounts of heavy metals that is deposited on plant canopy). Air pollution modeling is preferably used for human health risk assessment rather than foliar absorption of heavy metals by plants. Some models measure concentration of heavy metals which is emitted into the air from: (i) stationary sources (industrial units), (ii) mobile sources (vehicles) (iii) natural sources (windblown dust and wildfires), and area sources (road dust and fireplaces).

Recently, Stein et al. [312,313] developed HYSPLIT model to envisage the release, transfer, diffusion, and deposition of heavy metals and other air pollutants. Chen et al. [314,315] configured HYSPLIT to simulate the dispersion and deposition of particulate matter in air released from industrial point sources. United States Environmental Protection Agency (US EPA) developed the Human Health Risk Assessment Protocol (HHRAP) model for risk assessment and foliar metal transfer predictions for large-scale farms. However, HHRAP is not capable to predict heavy metal pollution in urban areas for kitchen gardens. Schreck et al. [316] developed a new model, “DECA”, which provides essential health risk assessment information regarding consumption of heavy metal polluted vegetables from kitchen gardens located in urban areas. However, till date, no specific model is developed which can trace link for heavy metal release from point sources (industries, traffic etc.), level in atmosphere, deposition/capturing of metals on plant leaves, foliar penetration inside plants. The development and installation of such models at community levels can be highly useful to predict risk associated with atmospheric pollution of heavy metals at certain periods and areas. Therefore, recommendations can be made based on the prediction of these models regarding the level of risk associated with the consumption of polluted crops.

12. Conclusions and perspectives

Despite considerable progress in recent years about knowledge on foliar absorption of heavy metals by plants, there exists yet exciting scientific areas to resolve particularly mechanisms involved for foliar absorption of metals by plants. Metal deposited on plant leaves enter the plants via penetration through the cuticle and stomatal openings. Heavy metal absorption by plant foliar parts depends on various factors, such as the physico-chemical properties of heavy metals and cuticle, the morphology, texture and surface area of plant leaves, exposure duration, and environmental conditions. Metal translocation within plants and contamination of edible parts mainly depends on the chemical metal species adsorbed on the leaf surface, plant maturity and cuticle composition.

After foliar uptake, metals undergo variation in their speciation due to changes of temperature, humidity at the leaf surface, phyllosphere activity and the interaction with various biochemical compounds. Studies reported contrasting evidences (positive, negative and neutral) regarding heavy metal toxicity to plants after foliar uptake. Data about the activation of defence mechanism after foliar metal uptake is almost missing. The mechanisms of metal uptake, translocation, compartmentation, toxicity and detoxification differ greatly for root and foliar metal pathways. However, a lot needed to be explored regrading heavy metal foliar uptake in the context of risk assessment studies, especially in areas near mining activities. Developments in this field will need a comprehensive understanding of the chemical, physical, biological, physiological and environmental processes and factors that control the uptake of foliar deposited heavy metals.

As shown by Dumat et al. [317], urban gardens are sometime set up in areas which look clean, even with metals measurement in soil, but the analysis of pollutants in water or atmosphere finally revealed high contamination. Consequently, when a land is sought for UPA projects, a global survey of the area should be mandatory to ensure health security. Preventive measures before opening new gardens, and modelling approach of the relationship between metals in plants and the various media is a major field of study. The quality of plants grown in urban and peri-urban areas is the result of many factors. Faced with this complex reality and the need to provide answers to citizens who want to eat healthy plant and grow vegetables preserving the environment, the concept of simplexity and multidisciplinary collaboration and multi-actors are highly relevant. They allow to set-up a collective intelligence approach conducive to the success of urban agriculture projects that require multiple steps and skills because of conflicts of land uses in urban areas and the sources of heavy metals. The discovery of pollution if it still generates initially legitimate questions and concerns on the part of the people concerned can also produce positive momentum for the realization of sustainable projects. To do this, a better knowledge by citizens of soil-plant-atmosphere transfer of pollutants and nutrients is essential to streamline the risks. It is an objective of the Network-Agriville (http://reseau-agriville.com/) which provides information, educational resources and a forum for various stakeholders in urban agriculture.

Based on the data summarized in this review article, the following research gaps need to be explored:

- Metal speciation plays an importing role in determining biochemical behavior of a metal. A detailed research is required about the role of metal speciation in term of foliar uptake, toxicity, compartmentation and detoxification inside plants.
- Heavy metal speciation in ambient air and the role of different industrial processes with respect to speciation of emitted heavy metals needs more detailed studies.

- The mechanism of heavy metal entrance to leaves via foliar transfer is not well-developed. Studies at molecular levels are required to explore foliar uptake of heavy metals.
- The role of different carrier genes and proteins involved in metal transfer and detoxification after foliar uptake needs to be explored. It is not clear whether vacuolar sequestration of heavy metals takes place after foliar absorption or not.
- Although, it is well-established that foliar metal transfer greatly varies with plant species, but there exist no classification (hyper-accumulator, tolerant, sensitive etc.) of plants species with respect to foliar transfer of heavy metals.
- After foliar uptake, heavy metals can cause overproduction of ROS, which impede with plant metabolism. However, the mechanisms of actions behind ROS overproduction and their harmful effects are still not explored for foliar metal transfer. Similarly, toxic effects of heavy metals after foliar uptake are not clear yet.
- The detoxification role of organic ligands (such as glutathione, methionine, phytochelatins, vitamins, proteins and amino acids) and antioxidative enzymes (SOD, CAT, APX, GPOX etc.) is not fully elucidated for foliar metal transfer.
- Certain heavy metals (Cd, Ni etc.) show hormetic effect (growth improvement at low applied levels, while toxicity at high applied levels) in plants, but the mechanisms as well as the threshold, upper and lower limit values for heavy metals of ambient air are not well-established for foliar metal transfer under different environmental conditions.
- There exist very low data regarding metal-induced human health risks via consumption of metal-contaminated food after foliar transfer, especially for urban agriculture.

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